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REACTIONS OF OZONE WITH ORGANICS IN AQUEOUS SOLUTIONS

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16. ABSTRACT

Rates of ozonation of some organic pollutants in the aqueous phase were studied. Experiments were conducted in distilled water with pH varying between 2 and 7; the solution temperature ranged from 5°C to 35°C.

Aromatic amines were very reactive with ozone and the reactions were second order. The rate of the naphthylamine/ozone reaction increased with temperature. The aniline/ozone reaction was faster, but was unaffected by temperature changes.

The toluene/ozone reaction exhibited a moderate rate. The order of the reaction changed with pH changes. PAHs including naphthalene, anthracene, and phenanthrene reacted with ozone according to second order kinetics. The reaction between ozone and anthracene was the fastest of all systems studied and the reaction rate was nearly independent of acidity.

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ABSTRACT

Rates of ozonation of some aromatic pollutants in the aqueous phase were studied by the stopped-flow technique. The kinetic experiments were conducted in distilled water and in aqueous solutions of pH values ranging from 2 to 7 at 5 to 35°C.

Aromatic amines including aniline and α-naphthylamine were very reactive with ozone and the ozonation reactions were second order. The rate of α-naphthylamine-ozone reaction was enhanced by temperature, but the faster reaction between aniline and ozone remained at a nearly constant rate for all temperatures.

The order of reaction between toluene and ozone varied with acidity though the rate of reaction was moderate. Polycyclic aromatic hydrocarbons including naphthalene, phenanthrene and anthracene were reactive with ozone according to second order kinetics. Rates of the naphthalene-ozone and phenanthrene-ozone reactions increased as the temperature increased and acidity of the solutions decreased. The reaction between anthracene and ozone was the fastest among the systems investigated, and the rate of reaction was nearly independent of acidity.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ac	--alternating current
A/D	--analog to digital
^{o}C	--degree centigrade
cm	--centimeter
dc	--direct current
kcal/g mole	--kilocalorie per gram mole
l	--liter
M	--molar or moles of solute per liter of solution
M^{-1} cm^{-1}	--per molar per centimeter
M^{-1} s^{-1}	--per molar per second
nm	--nanometer
pH	--logarithm of the reciprocal of hydrogen ion concentration in gram atoms per liter
pKa	--logarithm of the reciprocal of dissociation constant
psig	--pound per square inch at gauge pressure
s	--second
ms	--millisecond
v	--volt

SYMBOLS

A(t)	--absorbance as a function of time
b	--length of light path
C_A	--concentration of ozone
C_{AO}	--initial concentration of ozone
C_B	--concentration of organic reactant
C_{BO}	--initial concentration of organic reactant
C_i	--concentration of component i
HCl	--hydrogen chloride
H_2O	--water
H_3PO_4	--phosphoric acid
I	--ionic strength
I_2	--iodine
k_1	--rate constant for decomposition reaction
k_2	--rate constant for ozonation reaction
k	--reaction rate constant
k'	--apparent rate constant
KI	--potassium iodide
KOH	--potassium hydroxide
l	--order of decomposition reaction of ozone
m	--order with respect to ozone concentration in ozonation reaction
n	--order with respect to concentration of organic reactant in ozonation reaction
NaH_2PO_4	--sodium dihydrogen phosphate
Na_2HPO_4	--disodium hydrogen phosphate

NaI	--sodium iodide
NaOH	--sodium hydroxide
$Na_2S_2O_3$	--sodium thiosulfate
$Na_2S_4O_6$	--sodium tetrathionate
O_2	--oxygen
O_3	--ozone
t	--reaction time
v	--voltage
Z_i	--number of ion charges for component i
ε	--absorption coefficient
τ	--time constant

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SECTION 1

INTRODUCTION

Aromatic compounds are among the major pollutants emitted into the atmosphere from mobile and stationary sources such as automobiles, petroleum refineries and chemical manufacturing and fuel combustion facilities (25-27, 29,30). Although atmospheric organics vary considerably in structure, many species are reactive and may be oxidized to form secondary and tertiary pollutants. One of the most important oxidizing agents in the atmosphere is ozone produced in photochemical reactions in troposphere and stratosphere (26). A fraction of the ozone diffuses into the troposphere and contributes to the background ozone concentration. Oxidation of the organic compounds by ozone in vapor and liquid phases can result in formation of hazardous and/or toxic products (2, 3, 25). Under overcast, high-humidity conditions, dissolved organics may be oxidized in the liquid phase to produce secondary and tertiary pollutants (26). Rates and mechanisms of the conversion, however, are not well known. The present research, therefore, was undertaken to investigate kinetics of oxidation of toluene, naphthalene, phenanthrene, anthracene, aniline, and α-naphthylamine by ozone in aqueous media.

A stopped-flow spectrophotometer (Durrum Model D-110) was applied to conduct the kinetic experiments in distilled water and in aqueous solutions of various pH values and temperatures. Absorbance data were collected through an automatic data acquisition system interfaced to the spectrophotometer. Effects of the temperature and acidity on the oxidation rate were investigated.

SECTION 2

CONCLUSIONS

Aromatic amines can be very reactive with ozone as well as reagents of buffer solutions. In distilled water, aniline reacted with ozone according to second order kinetics, and the reaction rate constant is nearly independent of temperature between 10 and 35°C at 2.4×10^5 1/M-s. The reaction between α-naphthylamine and ozone was slightly slower; the second order rate constant is enhanced by temperature increasing from 0.53×10^5 to 1.3×10^5 1/M-s in the temperature range of 5 to 35°C.

The present research confirmed that polycyclic aromatic hydrocarbons in general are more reactive than simple aromatic hydrocarbons with ozone in the aqueous phase oxidation. Of the aromatic compounds investigated, the reaction between anthracene and ozone was the fastest with the second order rate constant of about 2×10^7 1/M-s in acidic solutions. The ozonation of phenanthrene also was fast and the rate constant increased with the pH value and temperature. At 25°C, the second order rate constant increases from 1.94×10^4 to 4.75×10^4 1/M-s as the pH value varies from 2.2 to 7.0. The second order reaction between naphthalene and ozone was moderate with the rate constant varying from 850 to 3750 1/M-s in the pH range of 3 to 7 at 25°C. As expected, the rate of ozonation of toluene was slowest among the oxidation reactions of aromatic hydrocarbons investigated. Similar to the ozonation of benzene, the order of reaction of toluene changed with acidity indicating a possible shift in the mechanism of reaction.

SECTION 3

RECOMMENDATIONS

Kinetic studies of oxidation of aromatic and olefinic compounds in aqueous media should be continued. The results of this work suggest that many organic pollutants are very reactive with ozone and that the rate of aqueous phase reaction can be much faster than the reactions in vapor phase. The kinetic information is needed in determining reaction life times and rates of degradation of individual aerosols or hazardous and/or toxic pollutants. Products of the ozonation, and mechanisms of the oxidation should be determined. Results of those studies can provide basic knowledge required for development of control strategies for individual organic pollutants.

Absorption of ozone in water drops and subsequent reactions between dissolved ozone and contaminants in the liquid phase may play important roles in determining the transport and fate of individual pollutants . Although, much attention has been focused on the vapor phase reaction, the results of the present research suggest that the gas-liquid reactions can be very important in the pollution control because of enhancement of the mass transport by the aqueous phase reaction. Theoretical and experimental investigation of the mass transport and chemical reactions in gas-liquid systems are recommended to provide the vital information.

SECTION 4

MATERIALS AND EQUIPMENT

PRODUCTION OF OZONE GAS

Ozone gas was produced by passing a stream of extra dry oxygen through a Welsbach Model T-408 Laboratory ozonator. The ozonator is operated on the corona discharge principle by imposing a high ac voltage across a gap in the presence of an oxygen-containing gas.

$$3O_2 \longrightarrow 2O_3 \qquad (1)$$

The efficiency is very low by this method, because only about 10% of the energy is utilized to produce ozone. The remainder is converted to light, sound and primary heat and, therefore, heat has to be removed by a water cooling system. Otherwise, a build-up of high temperature in the discharge space will reduce the yield of ozone since decomposition of ozone is very temperature sensitive. The concentration of ozone produced by the ozonator is affected by several factors, including flow rate of the gas stream, voltage, gas pressure, impurity of the gas stream and temperature of the cooling system (18, 21, 23, 28, 33). Water is not allowed in the ozone producing chamber, and therefore, the use of extra dry oxygen of -60°F dew point is recommended.

The ozonator is operated on 115 volt, 50/60 cycles, single phase power supply. The oxygen gas pressure has to be regulated to 10-18 psig and adjusted at 5-8 psig in the ozone producing chamber. The gas stream can be adjusted and measured at a flow rate between 0.5 to 2.0 l/min. The voltage can be set between 70 to 115 volts depending on the desired concentration of

ozone. Tap water is used in the cooling system. To achieve a high concentration of ozone in the gas stream, a small flow rate, high voltage and pressure, and low temperature of the cooling system should be applied.

The ozone outlet is first connected to an empty washing bottle then to a second washing bottle containing an appropriate buffer solutions. The remaining ozone is allowed to pass through a third empty washing bottle then absorbed in potassium iodide solution contained in a fourth bottle. The use of Tygon tubing, a good ozone resistant flexible material, is recommended for all connections in the output streams from the ozonator.

PREPARATION OF BUFFER AND AQUEOUS SOLUTIONS

Buffer solutions were prepared by adding appropriate amount of ACS grade chemicals such as HCl, NaH_2PO_4, Na_2HPO_4, H_3PO_4 or NaOH in distilled water for control of pH value and ionic strength. Any contaminants in the distilled water were oxidized by bubbling of ozone gas for at least 30 minutes and the residual ozone swept by nitrogen gas before preparing the buffer solutions.

Quantities of the various chemicals were determined from the following Henderson-Hasselbalch equation:

$$pH = pKa + \log(salt)/(acid) \qquad (2)$$

The ionic strength of a buffer solution is controlled by

$$I = 0.5\Sigma_i C_i Z_i \qquad (3)$$

where C_i is the molar concentration of component i, and Z_i represents the number of charges of ion for component i.

In the present research, pH values of the solution were controlled in the range of 2 to 7 and the ionic strength was maintained at 0.1 in all solutions. The pH value of a solution was measured by a Sargent-Welch Model NX pH meter. All buffer solutions were utilized within 2 weeks after preparation.

Highest grade chemicals available from various suppliers were purchased for this research. For each compound, a stock solution of a certain concentration was first prepared by dissolving appropriate amounts in 1000 ml of a buffer solution of desired acidity, and the mixed solutions stirred for 5 to 40 hours to achieve homogeneity. The stock solution was then diluted using buffer solutions of the same pH value to obtain reactant solutions with concentrations varying from 1.0×10^{-3} to 1.0×10^{-7}M. The solutions were kept in a cool and dark place, and used within a few days to avoid degradation.

STOPPED-FLOW SPECTROPHOTOMETER SYSTEM

The apparatus used in the kinetic experiments is a Durrum-Gibson Model D-110, stopped-flow spectrophotometer. It is a complete system for rapid mixing of two liquid reactants and for measurement of the change in optical absorbance as a function of time at a wavelength ranging from 200 to 800 nm. This system consists of six functional subsystems as shown in Figure 1. The subsystems are described below:

(1) The sample flow subsystem - includes reservoir syringes, drive syringes, valve blocks, sample mixing jet, observation cuvette and stop syringes.

(2) The flow actuating subsystem - initiates the sample flowing for each reaction run. The flow rate obtained from this system is 10 m/sec. A filtered air or nitrogen supply regulated at 70 psig is required.

(3) The optical subsystem - supplies monochromatic light by means of a light source and monochromator and routes it through the cuvette and into the photomultiplier tube.

(4) The electronics - provides power for all electrically operated components and calibrated readout/display processing for the measurement signal from the

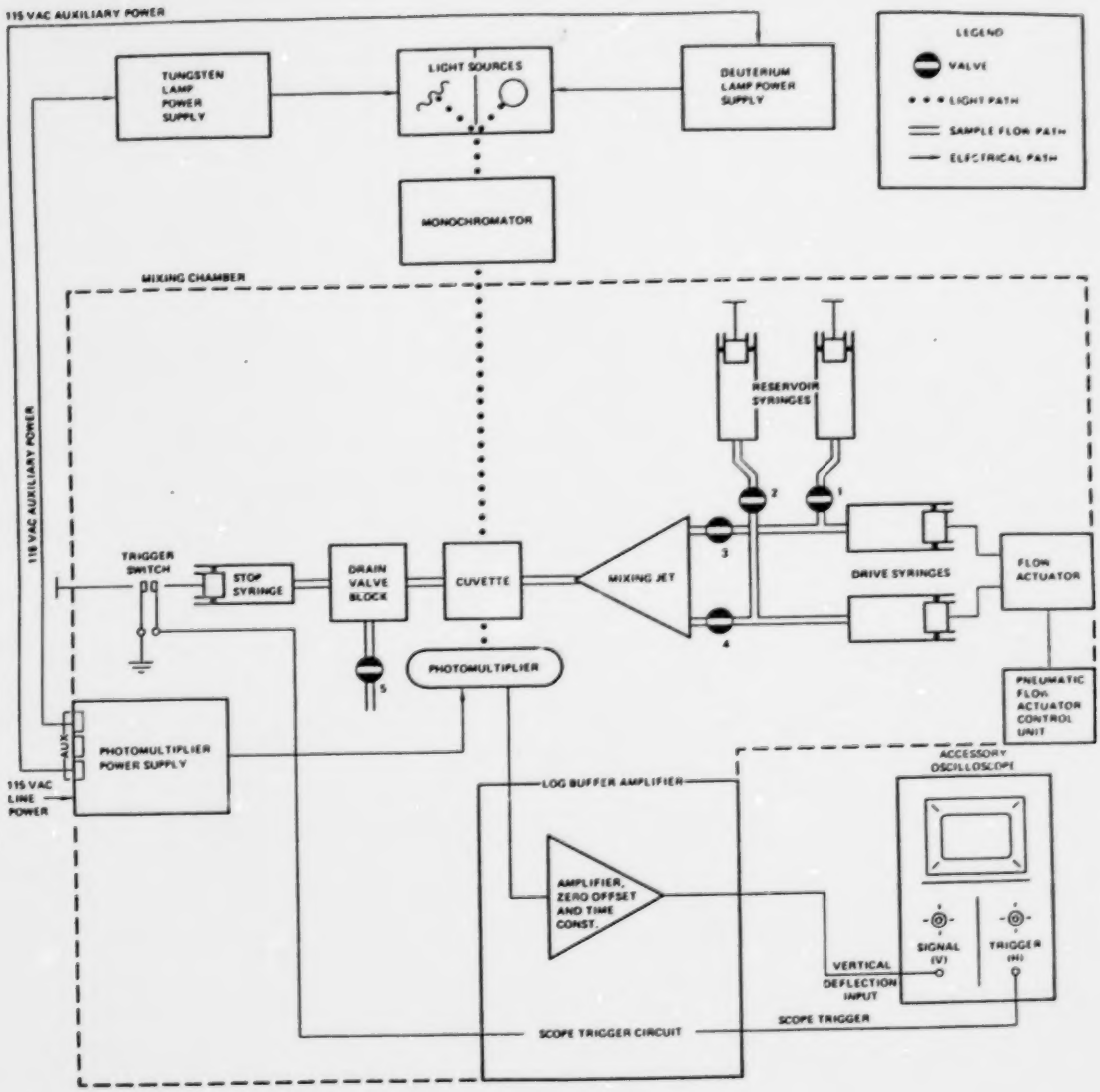


Figure 1. Functional Block Diagram of Stopped-Flow Spectrophotometer System

photomultiplier. The log buffer amplifier serves an important function for the signal display on the oscilloscope or input to the data acquisition system. A large time constant setting provides a stable signal but a slow response. On the other hand, a fast response but unstable signal can be obtained by using a small time constant.

(5) The temperature control subsystem - circulates a coolant (e.g. water) that maintains a constant temperature for all the parts of the flow subsystem. In the present research, a constant temperature bath, a Forma Scientific Model 2067 circulating system was used to maintain the circulating liquid at a desired temperature.

(6) Data recording devices - A Hewlett Packard 1207 A storage oscilloscope, a Model 198 A oscilloscope camera and a Model 680 strip chart recorder.

The kinetic experiments were conducted under isothermal conditions by water circulation through the stopped-flow spectrophotometer system to maintain a desired temperature. The stopped-flow equipment can be operated following appropriate valve settings and filling of two reactants in the drive syringes from the two separate reservoir syringes. Then, the valves may be reset for measurement of absorbance during a reaction. By activating the flow acturator,two solutions containing an organic compound and a solution of dissolved ozone in the two separate drive syringes can be forced to mix rapidly (99.5% complete within 0.0005 to 0.002 sec.) in the mixing jet and flow through the observation cuvette. Simultaneously, the light intensity signal from the photomultiplier tube, transmitted by passing a monochromatic light through the mixed solution in the cuvette observation chamber, is amplified and an output signal proportional to the absorbance (10 volts = 1 absorbance) is generated. The output signal is transmitted as function of reaction time to the oscilloscope or strip chart recorder for display and to

an automatic data acquisition system for collection, storage and analysis of the kinetic data.

DATA ACQUISITION SYSTEM

A data acquisition system for rapid kinetic experiments has been developed (15), utilizing the hardware components on loan from U.S. Environmental Protection Agency. A PDP 8M computer with A/D converter, tape drive unit and formatter, analog recorder, oscilloscope, and input/output terminal interfaced to the stopped-flow spectrophotometer provides the complete data acquisition system. Timing for actual data collection is generated through internal computer software with inclusion of A/D conversion time. The sampling time interval can be selected from the range of 1×10^{-4} to 100 sec. depending on the speed of a reacton. A total of 1943 data points can be collected and stored, and therefore, the total sampling time for a reaction can vary from 0.1943 to 1.943×10^{5} sec.

The system software, along with tape drive programs, is stored in core memory. All other machine language subroutines as well as high level programs are stored on tape. User-selected data, special analysis programs, and results are also stored on tape. Typical application of the system begins with a simple initialization from the computer console. After this start-up, software programming provides complete interaction between the user and the Decwriter III or teletype terminal. The user is directed through the process by a series of decision steps. The initial step is to choose a data file, either existing or new. Upon selecting the desired data file, a sequence of options is initiated, the first one being data collection. If an existing data file is chosen, the decision to write over this data is left open to the user. Should the data collection be negated, the existing data is transferred

from the tape to core memory for a series of print and analysis options. If data collection is assumed, various experimental parameters and timing constants are entered. After each run, the user may then decide whether to keep the new spectrum or return to re-initialize data collection for the same data file. A successful experiment may then be catalogued, and results printed out or stored on tape. At this juncture, the user can choose another data file or continue the print and analysis options. An IBM personal computer system also has been interfaced to the data acquisition system. The kinetic data for any experimental run, therefore, can be transferred to the IBM computer system for further correlations and analyses. The kinetic data obtained in this research were preserved and documented in several theses (23, 28, 33).

SECTION 5

EXPERIMENTAL PROCEDURES AND ANALYSES

DETERMINATIONS OF ABSORPTION COEFFICIENTS

Preliminary tests were conducted to determine the relationship between the absorbance of an ozone solutions measured by the spectrophotometer at a given wavelength and the actual concentration of ozone in the solution. The iodometric method was employed to determine concentrations of ozone in aqueous solutions. The oxidation of potassium iodide by ozone results in liberation of iodine which can be titrated by sodium thiosulfate solutions using starch as an indicator. The instantaneous reactions in the solution are as follows:

$$O_3 + 2KI + H_2O \rightarrow O_2 + I_2 + KOH \quad (4)$$

$$I_2 + 2Na_2 S_2 O_3 \rightarrow Na_2S_4O_6 + 2NaI \quad (5)$$

In a preliminary experiment, the absorbance of a buffer solution containing dissolved ozone at a fixed pH value and temperature was measured by the spectrophotometer at a given wavelength. Simultaneously, a portion of the solution was mixed with a solution containing excess potassium iodide. Since potassium hydroxide was produced, the mixed solution was acidified by sulfuric acid to maintain a pH value of 2 or below. The mixed solution was stirred continuously and titrated by the sodium thiosulfate solution until the yellow color of the liberated iodine nearly disappeared. As the colorimetric end point was approached, starch indicator was added to develop a dark blue color. The titration was continued until the blue color disappeared from the solution. The initial concentration of ozone in the solution, therefore, can be calculated from the amount of sodium thiosulfate consumed in the titration.

Absorbances of various concentrations of dissolved ozone measured at a

given wavelength indicated that a linear relationship existed between the absorbance, A, and the ozone concentration, C_A. This result suggests that the Beer's law is valid within the concentration range of interest.

$$A=\varepsilon bC_A \qquad (6)$$

In the above equation, the molar absorptivity or absorption coefficient, ε, at given wavelength with light path b=2 cm, can be obtained from the slope of the linear plot. The preliminary test also showed that temperature changes have negligible effect on the measured absorbances. The experiments were conducted at various wavelengths yielding the absorption coefficients or molar absorptivities as follows:

wavelength, nm	245	260	270	280
absorptivity, M^{-1} cm^{-1}	2,070	3,590	1,650	820

The above results are in good agreement with those reported in the literature (1, 16, 18).

SELECTIONS OF WAVELENGTHS

Careful selection of optimum wavelengths is an important consideration in the application of a spectrophotometer. In conducting a kinetic experiment, it is often advisable to select a wavelength at which absorbance is exhibited only by one of the reactants. This will allow applications of simple methods for analysis of measured absorbances. Also, the error introduced by the uses of the measured absorbances can be minimized without complications of the absorbance behavior exhibited by other reactants.

In experimental investigations of ozonation of organic compounds in aqueous solutions, it is desirable to conduct an experiment at a wavelength

where the absorbance of ozone is predominant in the aqueous solution. By conducting the experiment in this manner, it is permissible to analyze absorbances exhibited by ozone and reaction products only and neglect little absorbances of the organic reactants.

Since strong absorbances are exhibited by ozone in the aqueous phase in the wavelength range of 245 to 280 nm as shown in the previous section, attempts were made to conduct the kinetic experiments at a wavelength within this range. Therefore, preliminary tests were carried out to measure absorbances of individual organics in the aqueous medium at these wavelengths to aid in the selection of an optimum wavelength for the kinetic experiments. As illustrated in Figure 2 for aniline at a given concentration in distilled water, the absorbance approaches a minimum at 260 nm. Thus, the optimum wavelength of 260 was selected to study the aniline-ozone reaction. Similar tests were conducted for other organic reactants to determine the wavelengths selected in this project.

SELECTIONS OF TIME CONSTANTS

There is a selector switch in the stopped-flow spectrophotometer to choose one of the six filter capacitors to connect the signal path between the photomultiplier tube output and the log buffer amplifier. The output of the photomultiplier consists of a series of very minute pulses, whose time average is proportional to the transmittance of a sample. For a large time constant, the filter capacitor produces a very smooth curve on the oscilloscope display, but a rapid change in transmittance cannot be followed because of slow responses. A short time constant permits response to a rapid change in transmittance, but the oscilloscope display may contain a great amount of noises.

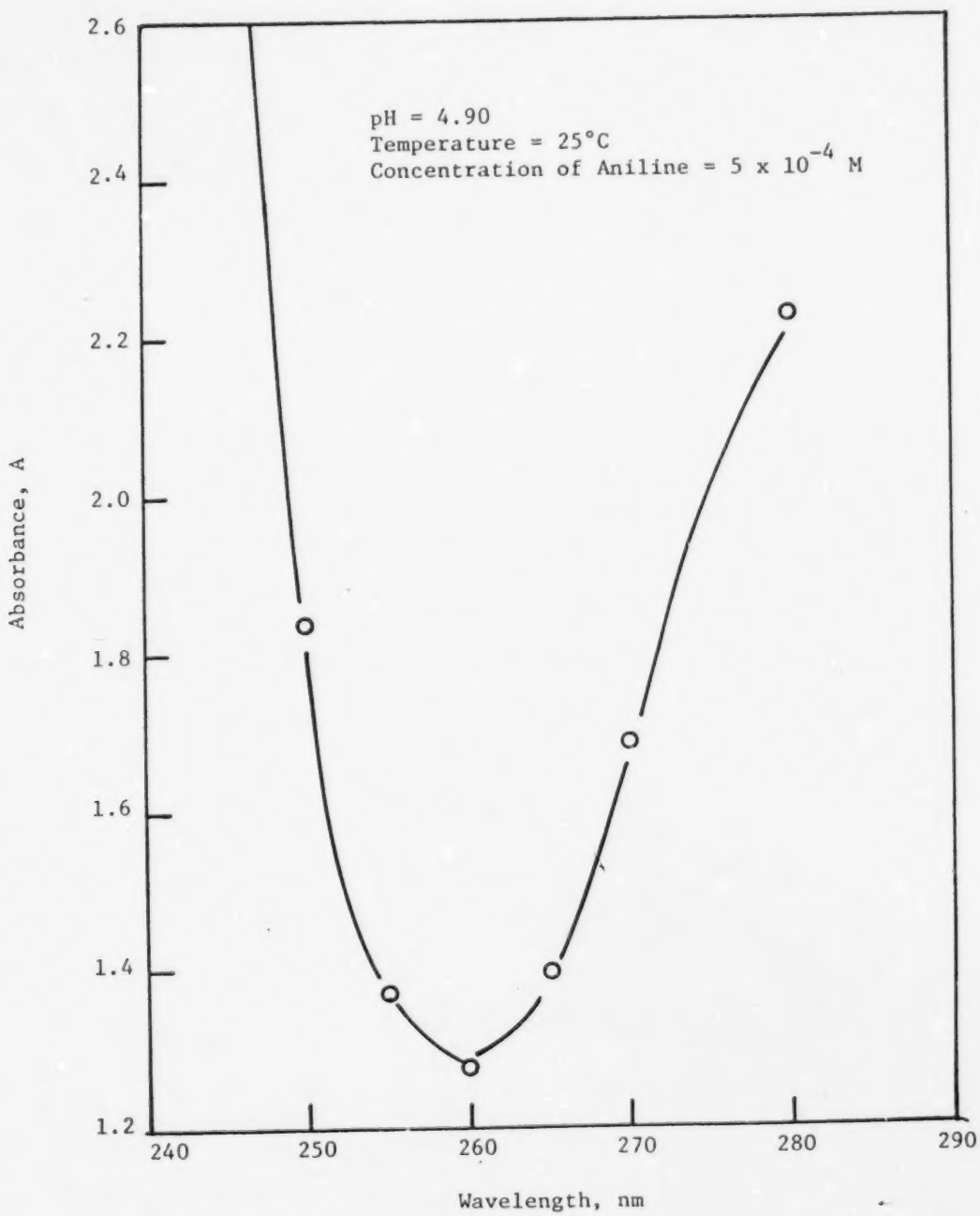


Figure 2. Absorbances of Aniline in Water at Various Wavelengths

Each filter capacitor is a first-order element, and its dynamic behavior is dictated by a first-order differential equation in time with a designated time constant, τ . The output voltage signal of a filter capacitor in response to a step change in an input voltage, ΔV_i, is then governed by

$$\Delta V(t) = \Delta V_i(1-\exp(-t/\tau)) \qquad (7)$$

As can be seen from the above equation, the dynamic response of output signal approaches unity exponentially. To achieve 99.9% response or higher, for example, the time required from the reaction experiment is $t \geq 6.9\tau$. This implies that for a filter capacitor of 10 ms time constant, 690 ms would be required before achieving more than 99.9% response. If the time constant of a filter capacitor is 1 ms, on the other hand, only 6.9 ms is needed to achieve the same or better response.

Although, a filter capacitor of small time constant is desirable as discussed above, the response signal may contain certain amount of noises. To compensate for this adverse effect, therefore, it is recommended to select a filter capacitor with a time constant about one-tenth of the reaction time constant. For example with a first order reaction of a rate constant, 10 s^{-1}, the reaction time constant is 1/10 second or 100 ms, and a filter capacitor with the time constant of 0.1 X 100 or 10 ms should be selected in conducting the experiment.

Some preliminary experiments for the reaction of toluene and ozone in neutral solutions were carried out using various filter capacitors to illustrate the effects discussed above (33). The experiments were conducted at 25°C, and absorbances of a reaction were followed at the wavelength of 280 nm. The absorbance changes with the reaction time are shown in Figure 3 for

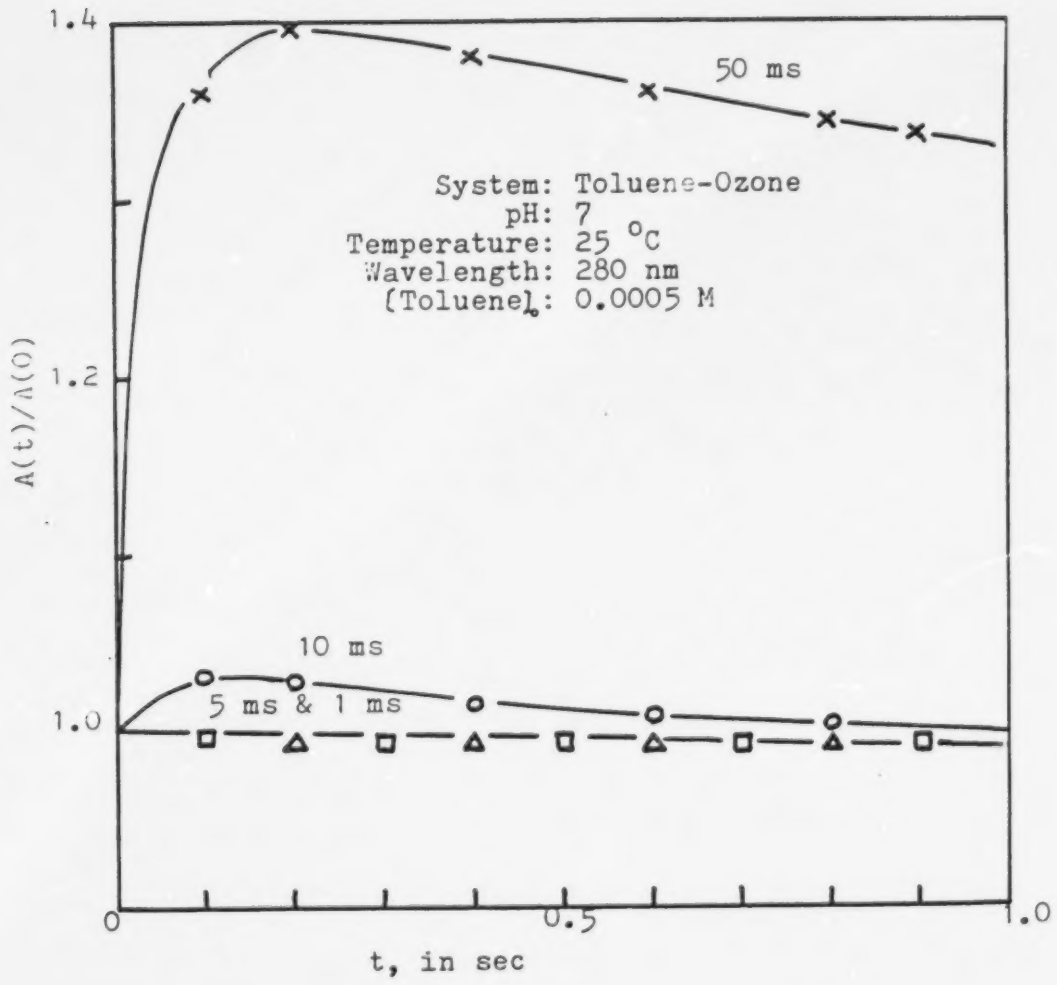


Figure 3. Absorbance Curves With Different Time Constants

four runs with time constant of the filter capacitors varying from 1 to 50 ms. Early portions of the absorbance data are plotted in Figure 4 to demonstrate the effect of the machine time constant on the absorbances measurements. The figure shows that the measured absorbance using the machine time constants of 1 and 5 ms declined with time, and that the absorbances increased with time for the filter capacitors of the time constants of 10 and 50 ms. These results clearly indicated that at the early period of the reaction, varying degrees of responses to the input signals were exhibited by using the capacitors of 10 and 50 ms, and that the observed absorbances should not be employed to calculate the reaction rate. On the other hand, the output signals from the capacitors of small time constants (1 and 5 ms) represented nearly full responses to the input signals even in the early period of the reaction. Consequently, these output signals with the time constants of 1 and 5 ms were true representation of the absorbances of the reaction solutions, and all kinetic experiments for the toluene-ozone system were conducted at the time constant of 1 ms.

KINETIC EXPERIMENTS AND ANALYSES

As described in a previous section, the stopped-flow spectrophotometer system was utilized for the kinetic measurements. An aqueous solution of ozone was prepared by bubbling a mixture of ozone and oxygen, produced from the ozonator, into a buffer solution contained in a Corning 3-040 gas washing bottle. The washing bottle was immersed in an isothermal bath to maintain a desired temperature. An organic solution was prepared from the buffer solution of identical pH value according to the procedures discussed earlier. The two solutions of ozone and organic reactants were stored in separate drive syringes in the stopped-flow spectrophotometer system prior to an experiment,

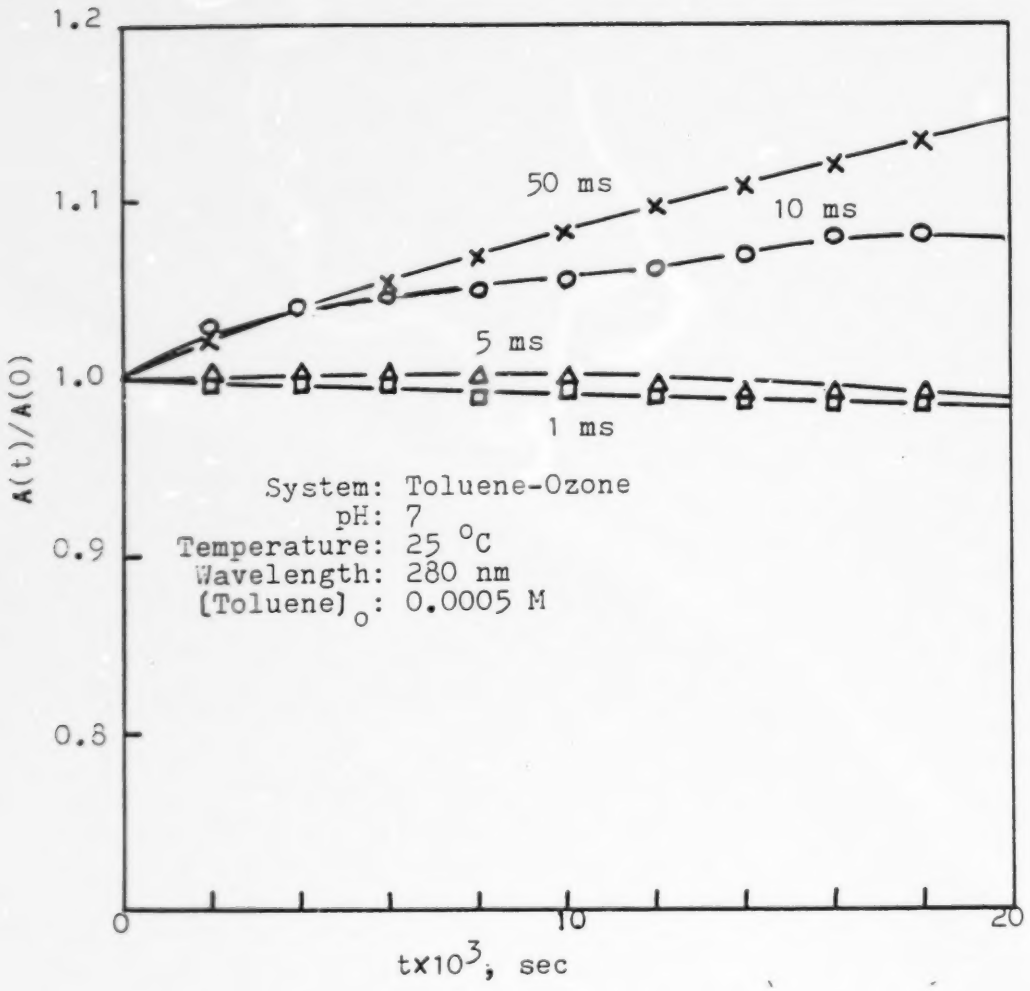


Figure 4. Absorbance Curves During Early Periods Of Reaction

and a constant temperature was maintained in the flow section by water circulation. By activating the flow actuator, the two reactants were mixed rapidly in the mixing jet and allowed to flow through the observation cuvette where the mixed solution was stopped abruptly. Absorbances of the mixed solution (as voltage in the output signals, 10 vdc per absorbance unit) were sampled at a fixed wavelength in a time interval varying from 1×10^{-4} to 100 sec. and stored in the PDP 8 M computer memories. The data acquisition system was applied using regression analyses to correlate the experimental data.

Table 1. Optimum Wavelengths and Time Constants

System	Wavelength, nm.	Time Constant, ms
Aniline - Ozone	260	5
α-naphthylamine - Ozone	260	1
Toluene - Ozone	280	1
Naphthalene - Ozone	245	1
Phenanthrene - Ozone	260	0.1
Anthracene - Ozone	245	0.1

Optimum wavelengths and time constants were selected in accordance with the procedures discussed earlier in this chapter. On the basis of the preliminary test the settings listed in Table 1 were selected to conduct the kinetic experiments for various systems.

Because of very low solubilities of naphthalene, phenanthrene and anthracene in water (22,31), the kinetic experiments for these systems were conducted in the aqueous solutions with ozone in large excess. For all other

systems, the organic reactants were present in excess in the aqueous media.

In the decomposition reaction of ozone (A) accompanied by an ozonation reaction between ozone and an organic reactant (B) in the liquid phase, the overall reactions can be expressed in the following forms:

$$A \xrightarrow{k_1} P_s \qquad (8)$$

$$A + bB \xrightarrow{k_2} Q_s \qquad (9)$$

The rate of depletion of ozone in the above simultaneous reactions can be written as

$$-dC_A/dt = k_1 C_A^{\ell} + k_2 C_A^{m} C_B^{n} \qquad (10)$$

where C_A and C_B are concentrations of the ozone and organic reactants, respectively, in the solution. Rates of decomposition of ozone were determined by many investigators (1, 13, 18) and the order of decomposition, ℓ, was found to vary from one to two. The rate constant, k_2, and orders of ozonation reaction, m and n, can be determined by analyzing the absorbance data obtained in this research.

The preliminary experiments indicated that the ozonation reactions for all systems were much faster than the rate of self-decomposition of ozone (18). The first term in the right hand side of equation (10), therefore, can be ignored in analyzing the kinetic data for the ozonation reactions. Under this

circumstance, the rate equation can be rewritten as

$$-dC_A/dt=(-1/b)(dC_B/dt)$$

$$= k_2 C_A^m C_B^n \qquad (11)$$

If the organic pollutant B is present in large excess in the solution, its concentration remains nearly constant during the ozonation reaction. Thus, equation (11) can be approximated by

$$-dC_A/dt = k' C_A^m \qquad (12)$$

where the apparent rate constant is

$$k' = k_2 C_{BO}^n \qquad (13)$$

Integration of equation (13) yields,

$$\ln C_A/C_{AO} = -k' t, \qquad \text{for } m = 1 \qquad (14)$$

and

$$(C_A/C_{AO})^{-m+1} = 1 - k'(1-m)C_{AO}^{m-1} \quad t, \quad \text{for } m \neq 1 \qquad (15)$$

In the above equations, C_{AO} is taken as the concentration of ozone at a time (0.0005 to 0.002 milliseconds) where complete mixing (>99.5%) of the reactants in the solution is achieved.

To apply the above integration method for analysis of absorbance data

obtained from a given experiment, it is necessary to establish a relationship between the absorbance and concentration of ozone in the solution. If no appreciable absorbance is exhibited by any chemical species other than ozone in the solution, then the concentration of ozone can be computed from equation (6) using the known value of the absorption coefficient for a given wavelength. For cases where absorbances of ozone as well as reaction products are significant and the ozonation reaction is controlled by an overall step indicated by equation (9) with negligible effect of the decomposition reaction, the concentration of ozone can be shown to vary with the absorbance of the solution as follows (12,18,21):

$$C_A(t)/C_{AO} = (A(t)-A(\infty)) \,/(A(o)-A(\infty)) \qquad (16)$$

where $A(\infty)$ is the asymptotic absorbance of the solution measured after completion of the ozonation reaction. By employing the relationship given in equation (16), the dimensionless concentration can be plotted against the reaction time on a semi-logarithmic or regular scale according to equation (14) or (15). Regression analyses can be utilized to find a best correlation of the experimental data yielding the reaction order m and the apparent rate constant, k'. By plotting k' versus the initial concentration of the organic reactant, C_{BO}, on a logarithmic scale, a straight line can be obtained where the slope gives the order with respect to the organic compound, n. Thus, the ozonation rate constant, k_2, can be computed from the intercept of equation (13).

For the phenanthrene-ozone and anthracene-ozone reactions, the experiments were carried out with ozone in large excess in the solutions. Equations (12) and (13) are replaced by

$$-dC_B/dt = k'C_B^n \qquad (17)$$

and

$$k' = k_2 \; b \; C_{AO}^m \qquad (18)$$

Integrated equations (similar to equations 14 and 15) can be derived, and the following relationship is valid (10,12):

$$C_B(t)/C_{BO} = (A(t)-A(\infty))/(A(o)-A(\infty)) \qquad (19)$$

Thus, the procedures outlined earlier also can be applied to analyze the kinetic data.

If the initial concentrations of ozone and the organic reactants are comparable, it is necessary to obtain a rate expression from direct integration of equation (11). For the second order reaction (m=n=1), the integrated equation can be derived as,

$$\ln (b+(C_{BO} - bC_{AO})/C_A) = \ln C_{BO}/C_{AO} + k (C_{BO} - bC_{AO})t \qquad (20)$$

Also, it can be shown that equation (16) is valid in relating the

dimensionless concentration of ozone, C_A/C_{AO}, with the absorbances of the solution (12). Knowing the stoichiometric ratio, b, and the initial concentration of the organic reactant, C_{BO}, the term in the left hand side of the above equation can be plotted against the reaction time, t. The slope of the straight line plot is k $(C_{BO} - bC_{AO})$. The absorbance data from the naphthalene-ozone reaction were analyzed by this procedure.

SECTION 6

RESULTS AND DISCUSSION

OZONATION OF AROMATIC AMINES

Aniline and α-naphthylamine were reactive with buffer reagents such as H_3PO_4, NaH_2PO_4 and HCl as indicated by results of the preliminary tests. Thus, the kinetic experiments were carried out in distilled water (pH values of 4.9 to 5.2) without buffer to eliminate interferences of the buffer reagents. The temperature of the reactions was controlled by water circulation in the range of 5 to 35°C. The absorbance data obtained for the systems are tabulated in a thesis (28).

Typical absorbance changes during the reaction of aniline and ozone are illustrated in Figure 5 for three runs. As shown in this figure, the absorbance of a mixed solution increased very rapidly during the very early period of 40-60 milliseconds and then declined slowly in the remaining period. This behavior tends to suggest the formation of intermediate products of high absorbances in the first period of the reaction and further reaction or decomposition of the intermediates in the remaining life of the reaction.

The kinetic data were analyzed according to the method outlined earlier. The absorbances measured during a reaction can be transformed into the ratio of ozone concentration at a given reaction time to its initial concentration, and the regression technique utilized to correlate the data. The results obtained for the three typical runs were plotted in Figure 6 to demonstrate that the absorbance data were best fitted by assuming a first order reaction with respect to the ozone concentration. The apparent rate constants for a given temperature, k', were calculated and plotted against initial

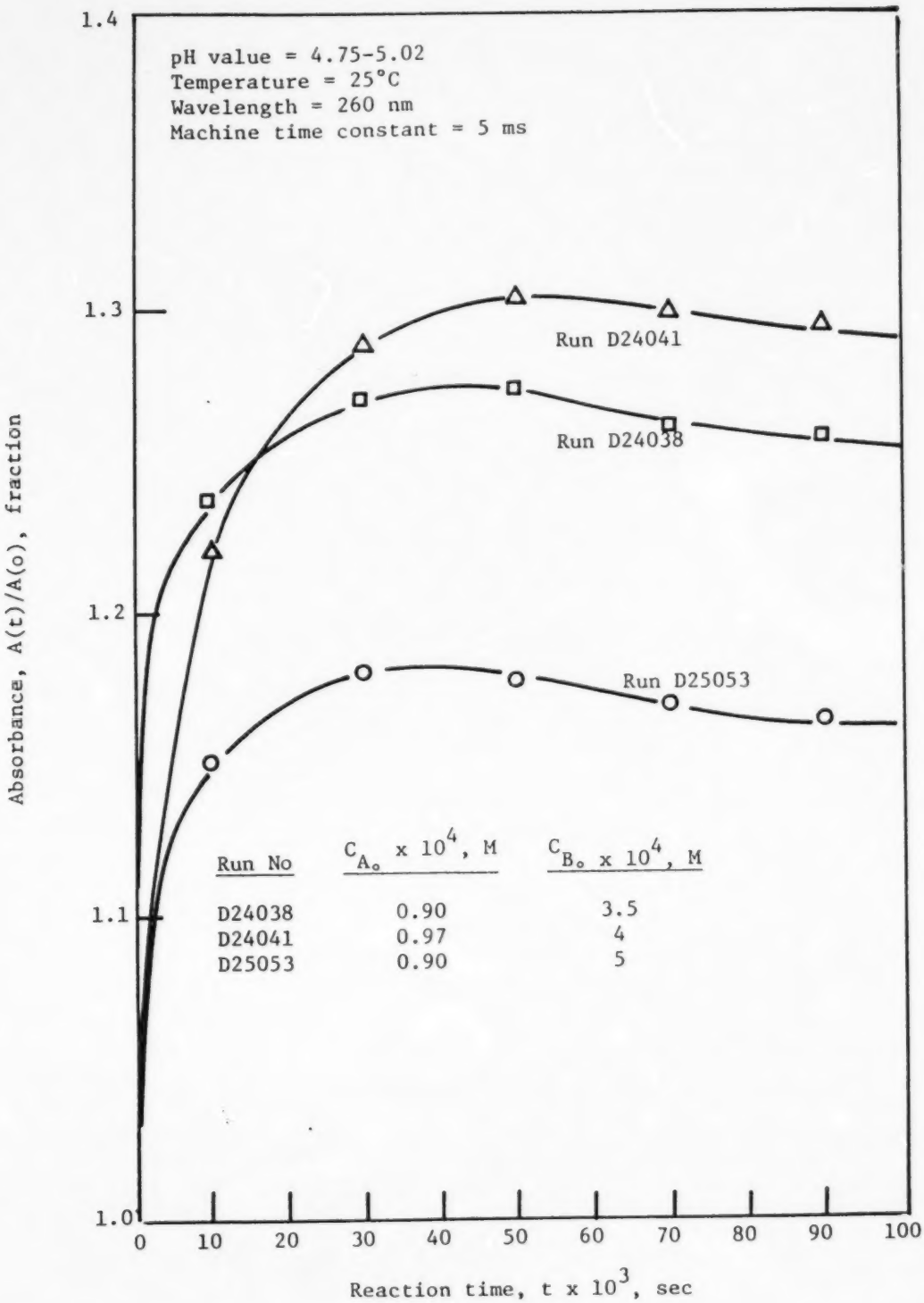


Figure 5. Absorbance Changes During The Aniline-Ozone Reaction

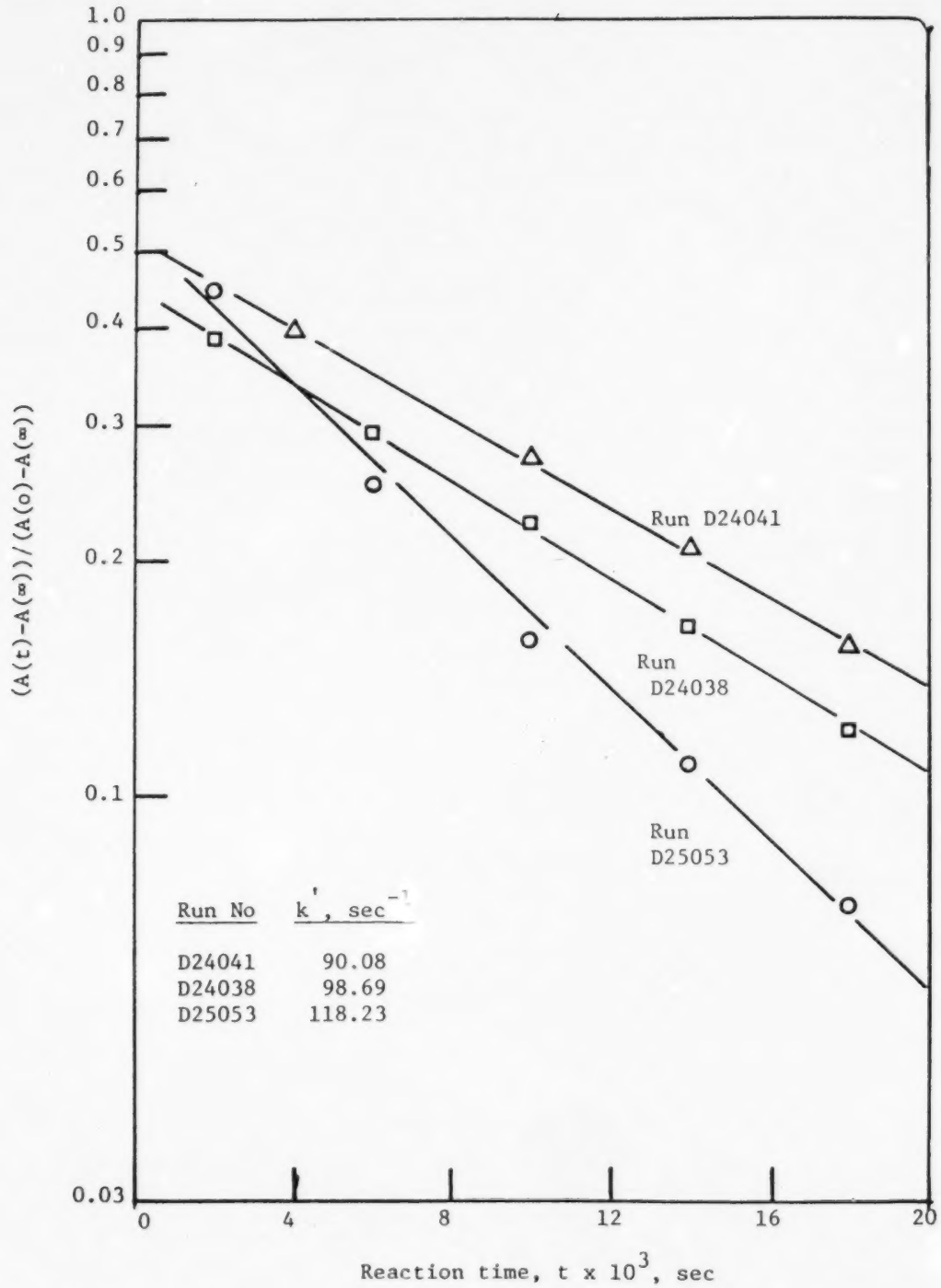


Figure 6. Determination Of Order With Respect To Ozone In The Aniline-Ozone Reaction

concentrations of aniline on a logarithmic scale as illustrated in Figure 7. The slope and intercept of the straight line were calculated, and the n value (order with respect to the aniline concentration) at 25°C was about 0.73. For practical applications, therefore, the ozonation reaction of aniline can be considered as first order with respect to concentrations of both ozone and aniline, and the average reaction rate constant is estimated to be 2.5×10^5 $M^{-1}s^{-1}$ at 25°C. Analyses of the kinetic data for the α-naphthylamine-ozone system also indicated that the overall reaction was second order with the rate constant of 1.3×10^5 $M^{-1}s^{-1}$ at 25°C.

Average rate constants for all experiments at various temperatures were computed as listed in Table 2. In the temperature range of 5 to 35°C, the rate constants vary from 9.4×10^4 to 2.47×10^5 $M^{-1}s^{-1}$ for the aniline-ozone reaction, and from 5.2×10^4 to 1.25×10^5 $M^{-1}s^{-1}$ for the α-naphthylamine-ozone reaction. Standard deviations of the correlated data range from 5 to 32%.

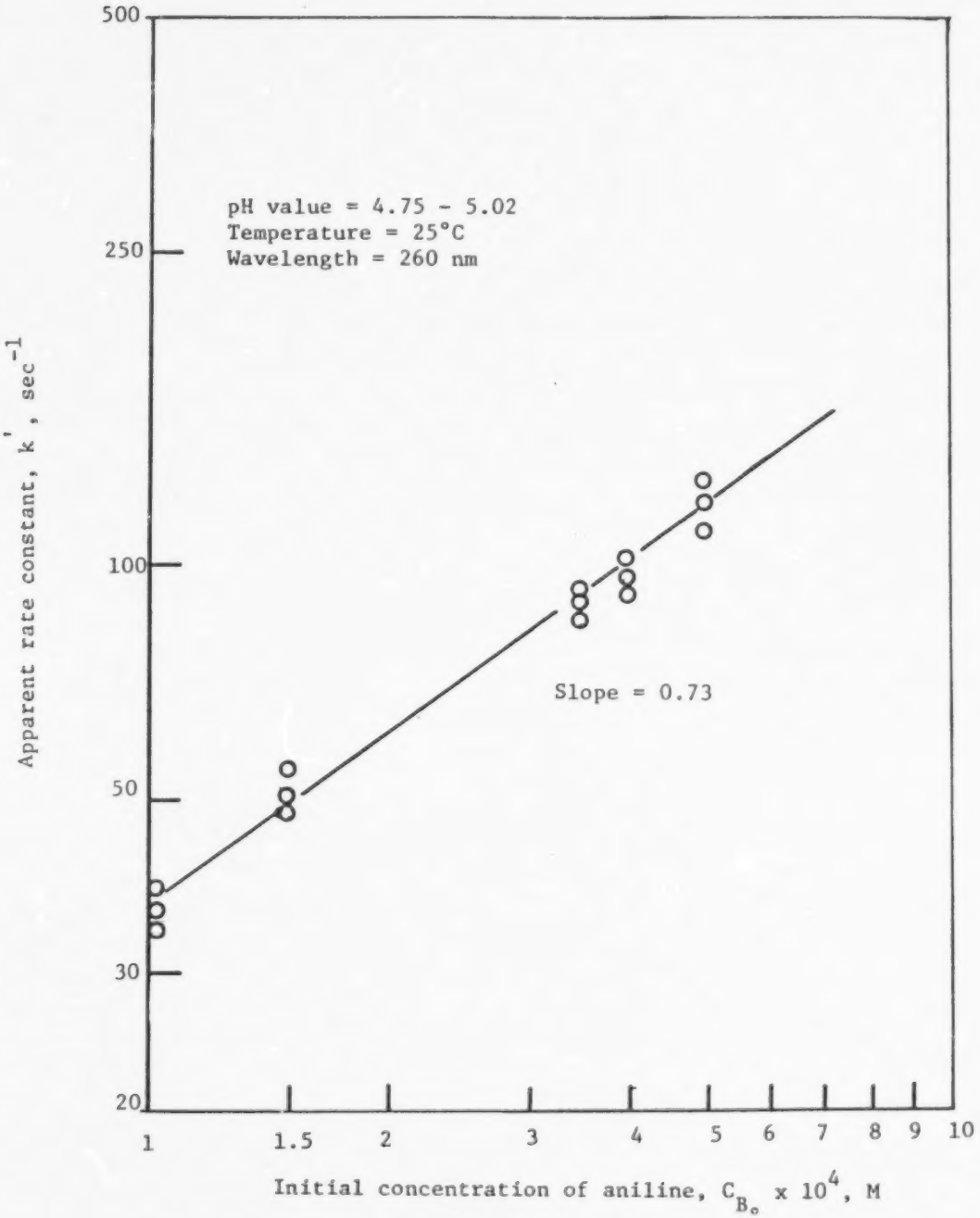


Figure 7. Determination Of Order With Respect To Aniline In The Aniline-Ozone Reaction

Table 2. Average Rate Constants for Ozonation of Aromatic Amines in Water

System	Temperature, °C	Rate Constant, 1/M-s
Aniline-Ozone	5.0	94,000
	10.0	230,000
	25.0	247,000
	35.0	231,000
α-naphthylamine-ozone	5.0	52,000
	10.0	75,000
	25.0	98,000
	35.0	125,000

As can be seen from the table, the rate constants for the aniline-ozone reaction remain nearly constant at about 2.4×10^5 $M^{-1}s^{-1}$ in the temperature range of 10 to 35°C. At 5°C, however, the rate constant drops sharply to 9.4×10^4 $M^{-1}s^{-1}$. For the α-naphthylamine-ozone reaction, on the other hand, the rate constant increases from 5.2×10^4 to 1.25×10^5 $M^{-1}s^{-1}$ as the temperature increases from 5 to 35°C. The Arrhenius equation can be applied to correlate this temperature effect as shown in Figure 8 yielding an activation energy of 4.4 kcal/gmole.

Aniline is more reactive toward ozone than many aromatic compounds because of the highly activating $-NH_2$ group. Mechanisms governing ozonation reactions of aromatic compounds have been discussed by many investigators (4,5,19,20,24,34,35). Similar to phenol, electrophilic ozone attack at ortho

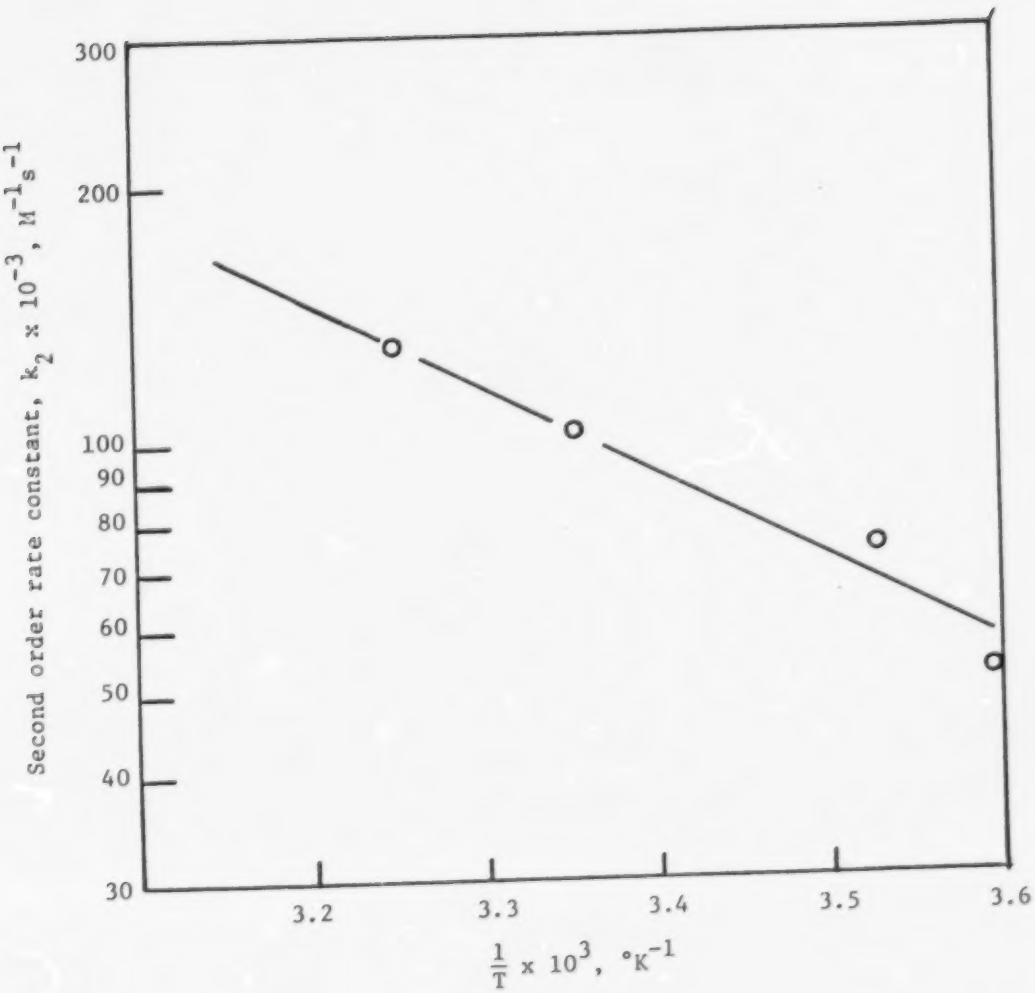


Figure 8. Effect Of Temperature On The α-Naphthylamine - Ozone Reaction

and para positions of the aniline ring may be possible, though Langlais, et al (20) suggested that the major attack occurred at the para position. In an earlier study of ozonation of phenol in aqueous solution, Li (21) found that the electrophilic attachment at the ortho position was the major mechanism to produce catechol and o-quinone.

In spite of the above possible difference in the position of electrophilic attack by ozone, absorbance behaviors of the two reactions, phenol-ozone and aniline-ozone, followed a similar trend. For both systems, the absorbance of a reaction mixture increased rapidly in the initial period and then declined gradually during the remaining life of the reaction. The overall kinetics of the ozonation reaction was second order with first order each in ozone and in the organic reactant. The second order rate constants obtained for the aniline-ozone reaction are larger than those calculated for the phenol-ozone reaction. For example, at 25°C, the average rate constant is $2.95 \times 10^4 M^{-1}s^{-1}$ for the ozonation of phenol in buffer solution of a pH value of 5.2 (21). On the other hand, this work yields the average second order rate constant of $2.47 \times 10^5 M^{-1}s^{-1}$ for the ozonation of aniline in distilled water (with the pH range of 5.02-5.20) at 25°C. This suggests that the aniline-ozone reaction proceeded at a rate much faster than the phenol-ozone reaction. Another interesting observation is that the phenol-ozone reaction was sensitive to temperature changes but the aniline-ozone reaction was nearly independent of temperature except at very low temperatures.

In the ozonation reaction of α-naphthylamine, the $-NH_2$ group acts as a powerful activating group (electron-releasing group)(34). Evidences (4,14) suggest that the ozonation reaction of α-naphthylamine is initiated by ozone attack at the ring containing the NH_2 group, and two molecules of ozone may be consumed in the electrophilic reaction to form a diozonide. Further reactions

with ozone or hydrolysis of the diozonide may be expected following the initiation step. If the initial attack of ozone is considered to be the major reaction controlling the depletion of ozone in a solution, then the overall reaction between ozone and α-naphthylamine may be considered second order as confirmed by the experimental results. A comparison of the rate constants for the aniline-ozone and α-naphthylamine-ozone systems reveals, however, α-naphthylamine is not as reactive as aniline with ozone in the aqueous phase.

Possible oxidation of aniline and α-naphthylamine by hydrogen peroxide in distilled water was also investigated. No appreciable changes in the absorbance of a mixed solution of the reactants was detected. This result suggests that neither aniline nor α-naphthylamine is reactive with hydrogen peroxide in distilled water without a catalyst.

OZONATION OF TOLUENE

Absorbance changes during the toluene-ozone reactions are shown in Figure 9 for several runs in aqueous solutions of various pH values. Correlations of the absorbance data by regression analyses revealed that the ozonation reaction was first order with respect to the concentration of ozone. As shown in Figure 10 for the apparent rate constant versus the initial concentration of toluene, the slopes vary depending upon the acidities of the aqueous solutions. The order with respect to the concentration of toluene can be considered unity (n=1) in the solutions of pH values of 2 and 3, one-half (n=0.5) at the pH value of 5.6, and nearly zero (n=0) in the neutral solutions. The reaction rate constants were calculated and documented in a thesis (33), and the average values are summarized in Table 3. Standard deviations of the correlations vary from 8 to 23%.

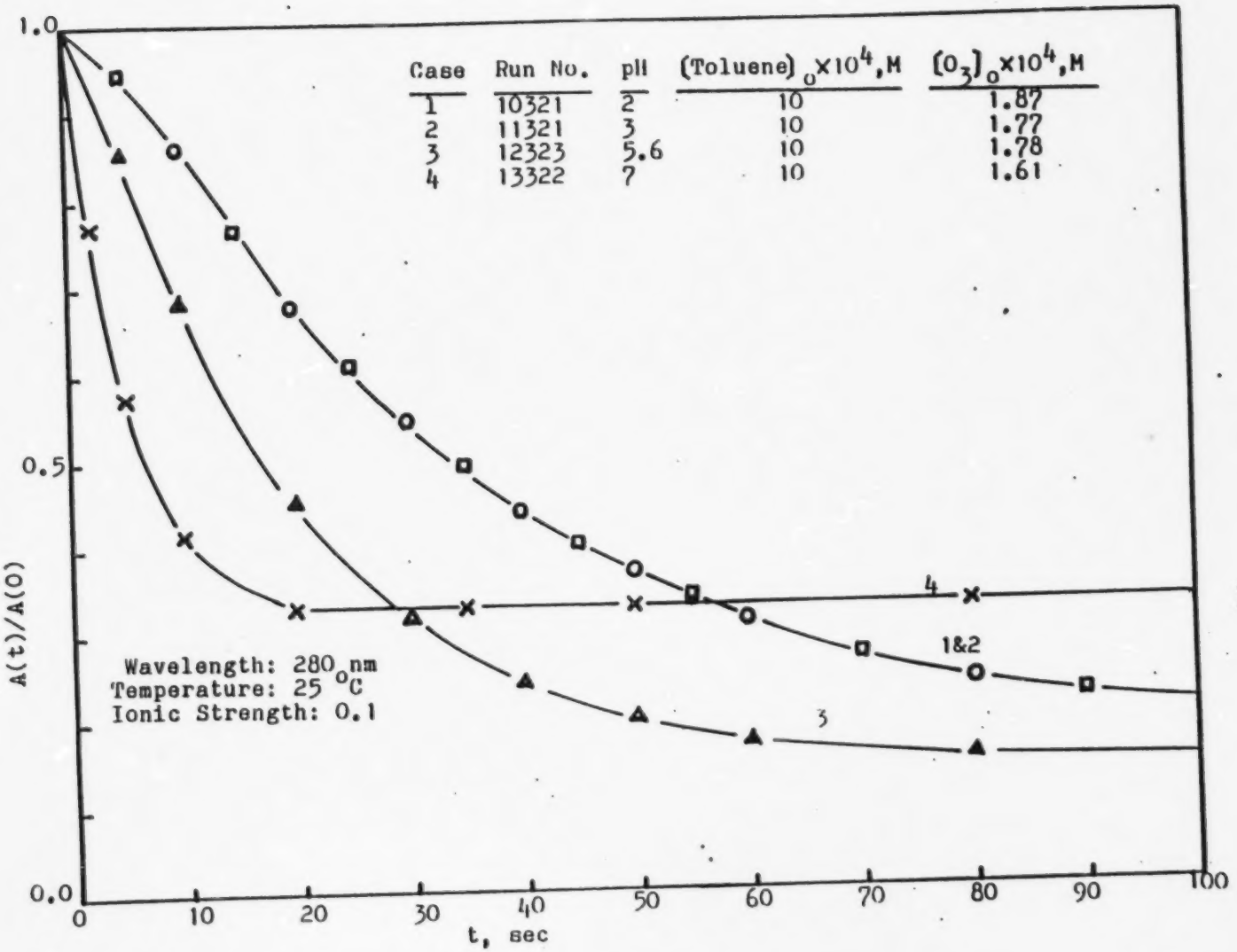


Figure 9. Absorbance Changes During The Toluene - Ozone Reaction

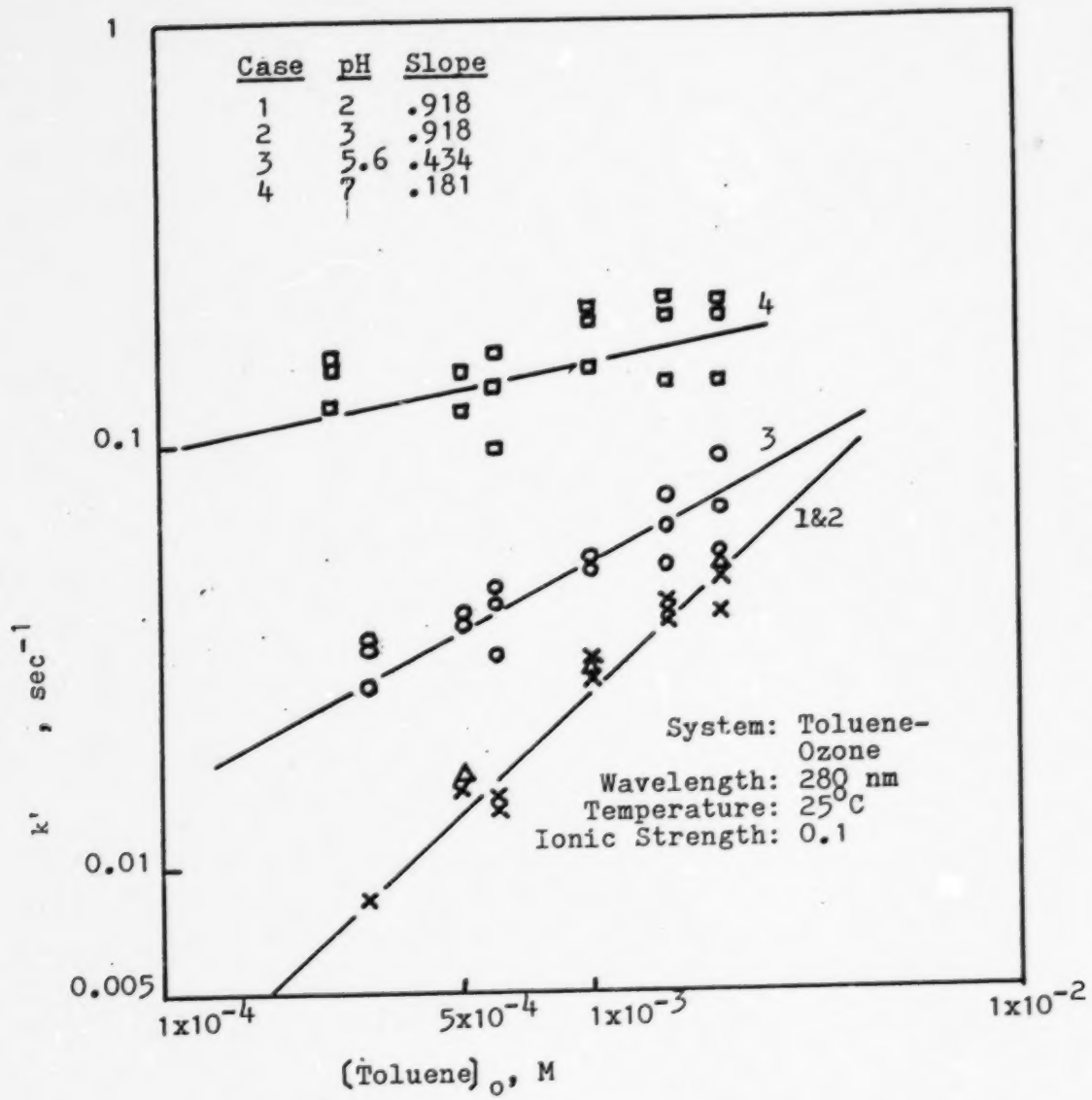


Figure 10. Determination Of Order With Respect To Toluene

The effect of the pH value on the average reaction rate constant is demonstrated in Figure 11 for experiments conducted at 25°C. This figure was prepared by converting the reaction rate constants at different pH values into the common unit of the second order rate constant. The figure shows that the reaction rates were relatively slow in strongly acidic solutions. For example, the second order rate constants vary between 27 to 29 $M^{-1}s^{-1}$ in the solutions of pH values of 2 and 3, with half reac ion life time of more than 20 seconds as indicated by the absorbance data tabulated elsewhere (33). The rate constant increases rapidly with the pH value, and in the neutral solutions, the second order rate constants are in the range of 97 to 228 $M^{-1}s^{-1}$ with half lives of less than 3 seconds. Therefore, the reaction in the neutral solutions was at least 3 times faster than the reaction in the strongly acidic solutions.

The Arrhenius equation can be employed to correlate the dependence of the rate constant on temperature as demonstrated in Figure 12 and 13. The figures illustrate that the influence of the temperature on the rate of ozonation of toluene is very significant, especially in the neutral solutions. The experimental results show that in the acidic solutions with pH values of 2 and 3, the reaction rate increases about twice for a temperature increase of 10°C. In the neutral solutions, however, the rate increases about 10 times for the same temperature change of 10°C.

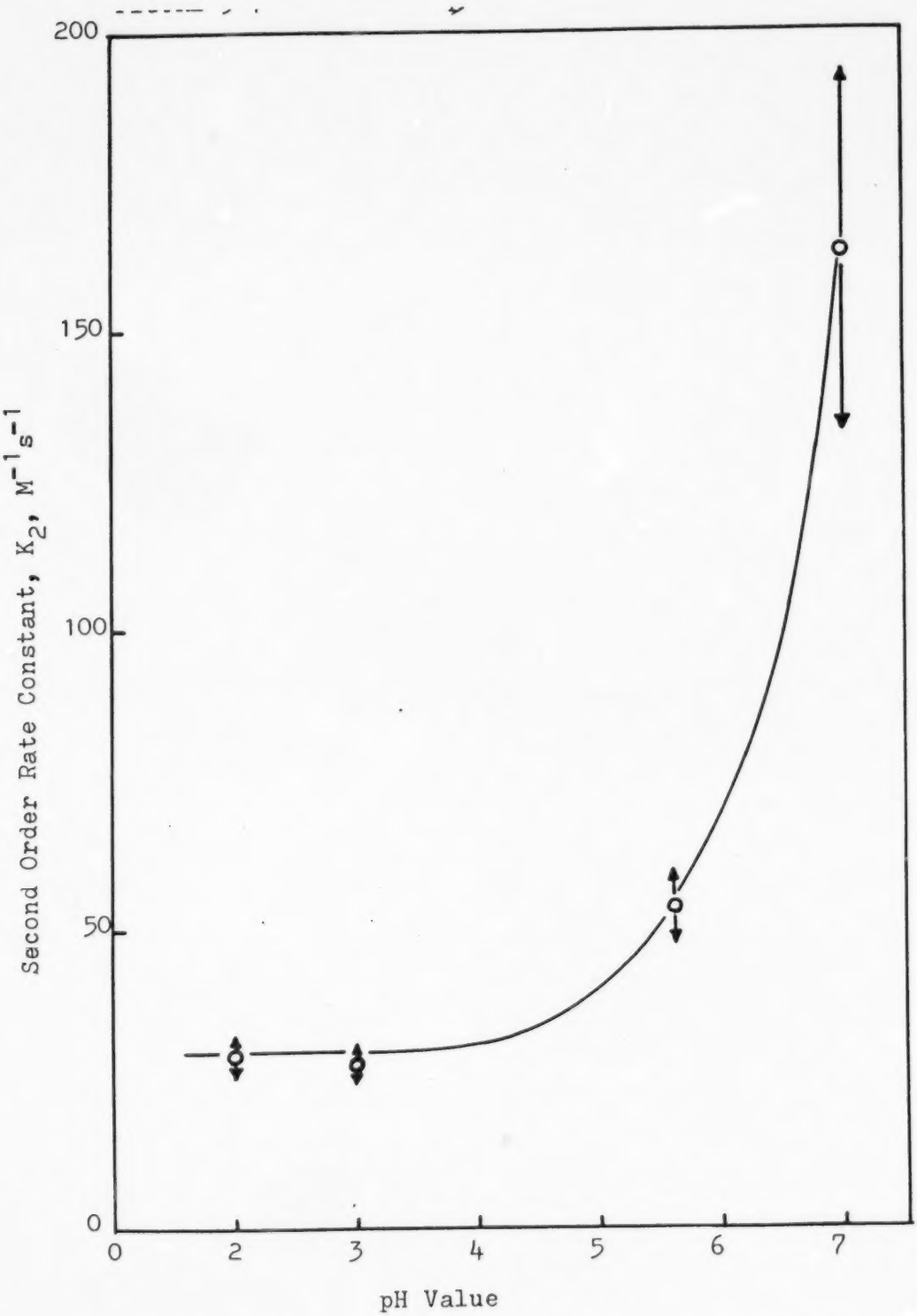


Figure 11. Effect Of Acidity On The Toluene - Ozone Reaction

Table 3. Average Rate Constants For The Toluene-Ozone Reaction

pH Value	Temp, ^{o}C	Order With Respect To O_3	Order With Respect To Toluene	Rate Constant, k_2
2	10	1	1	10.54 M^{-1} s^{-1}
2	25	1	1	29.25 M^{-} s^{-1}
2	35	1	1	53.30 M^{-1} s^{-1}
3	25	1	1	27.21 M^{-1} s^{-1}
3	35	1	1	53.18 M^{-1} s^{-1}
5.6	25	1	1/2	1.697 $M^{-1/2}$ s^{-1}
7	10	1	0	.01972 s^{-1}
7	25	1	0	.1634 s^{-1}
7	35	1	0	1.614 s^{-1}

The activation energies can be calculated from the slopes of the straight lines in Figures 12 and 13. At the pH values of 2 and 3, the activation energy was found to be 11.22 kcal/g mole with a frequency factor of 4.91×10^{9} $M^{-1}s^{-1}$. In the neutral solutions, the calculations yielded an activation energy of 31.26 kcal/g mole and a frequency factor of 1.79×10^{22} s^{-1}. The significant difference in the activation energies at various pH values suggest that the mechanism of ozonation of toluene might be different depending upon the acidity of a solution.

The ozonation rate of toluene was faster in the acidic solutions and slower in the neutral solutions than the benzene-ozone reaction (16.17). Nontheless, the changes in the reaction orders and the possible shift in the

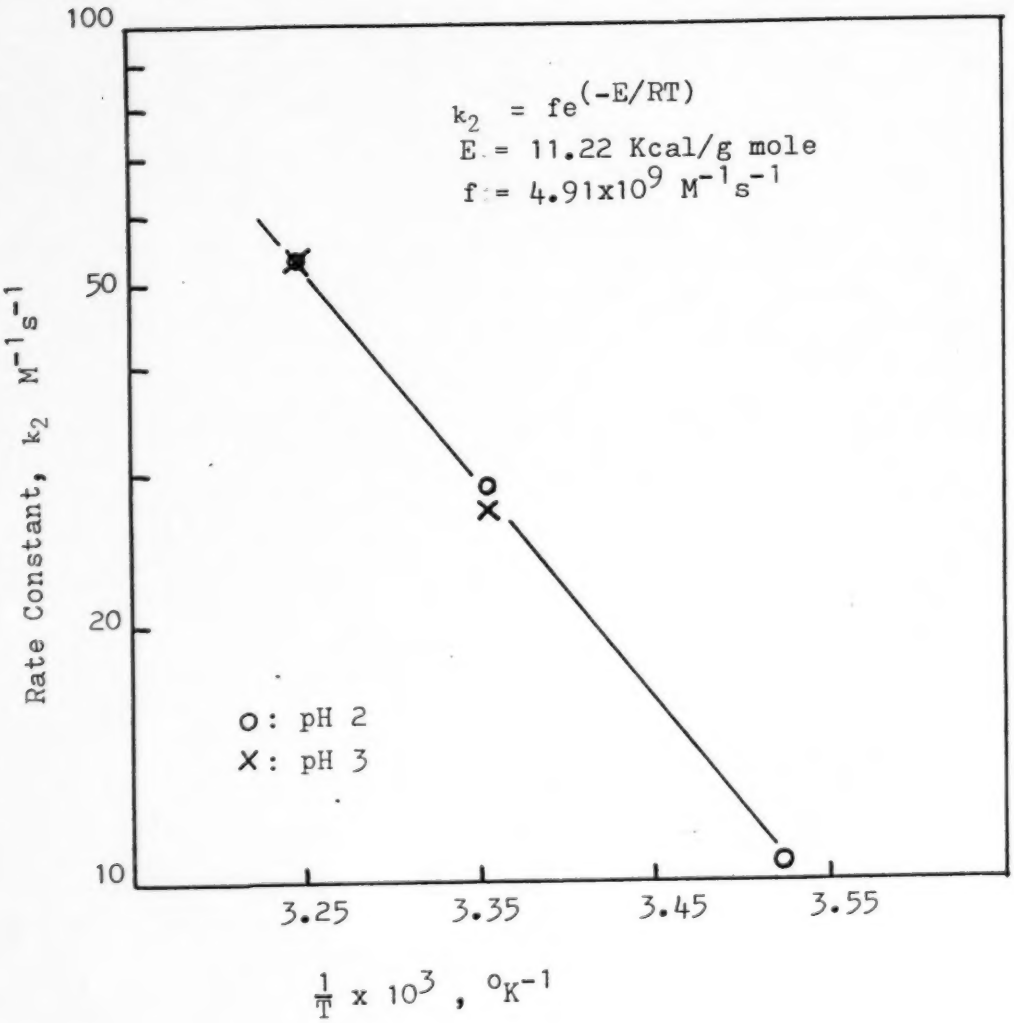
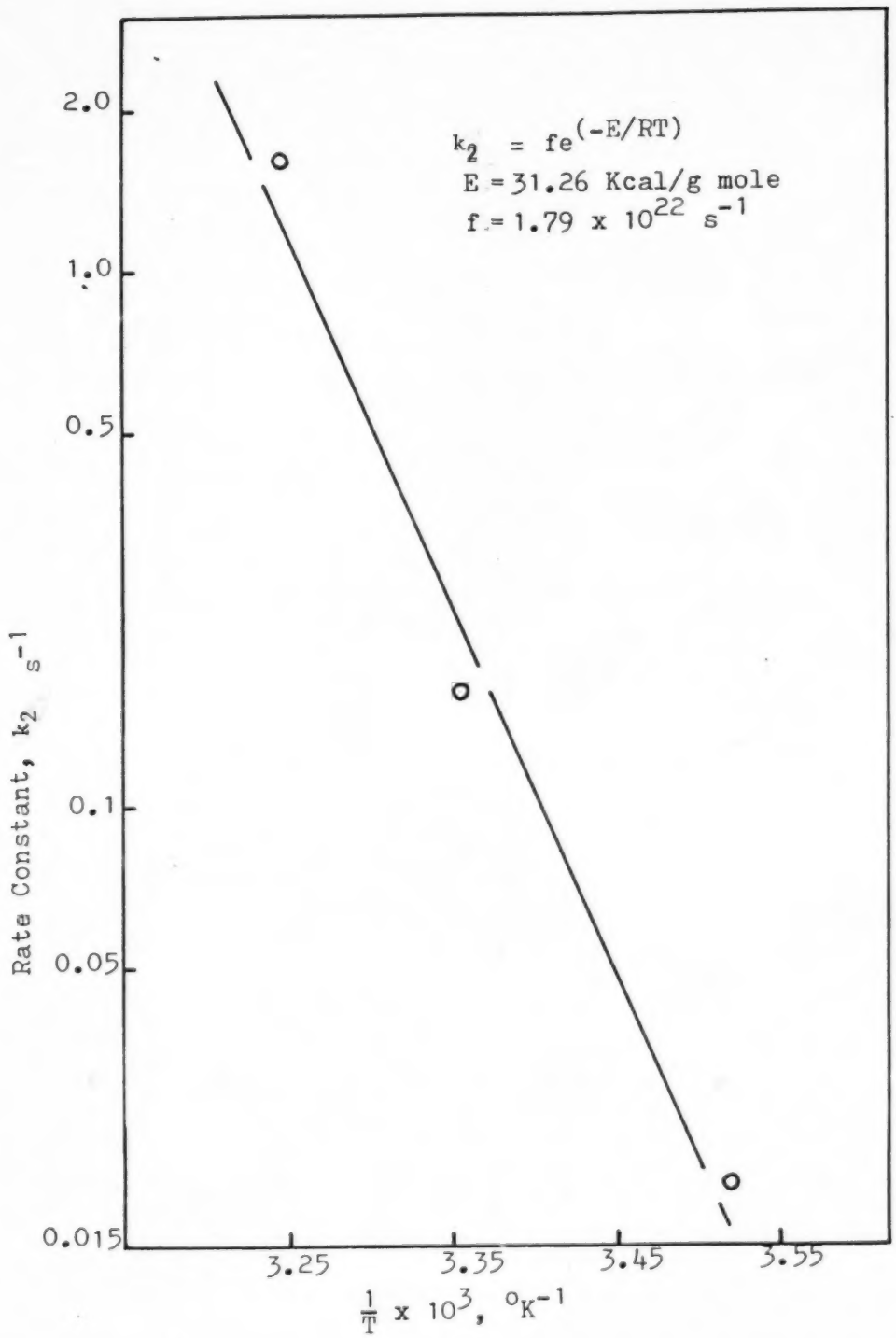


Figure 12. Effect Of Temperature On The Toluene - Ozone Reaction In Acidic Solutions

Figure 13. Effect Of Temperature On The Toluene - Ozone Reaction In Neutral Solutions



reaction mechanisms with the acidity were observed in the ozonation reactions of both benzene and toluene. In an investigation of ozonation of polyalkyl benzenes in organic solvents by Nakagawa, et al. (24), the rate constants were calculated assuming second order kinetics (first order each in ozone and in aromatic hydrocarbon). The ozonation reaction of toluene was very slow with the second order rate constant of 0.166 M^{-1} s^{-1} in carbon tetrachloride and 0.091 M^{-1} s^{-1} in acetic acid. Also, as reported in the literature (25), the ozonation rate constant in the vapor phase at 25°C is about 7 M^{-1} s^{-1}. The results of the present research indicated, however, the ozonation reactions in the aqueous media were faster than those in other environments reported by the previous investigators. The second order rate constants in the strongly acidic solutions (with pH ranging from 2 to 3) at 25°C are about 27 to 30 $M^{-1}s^{-1}$. The rate constant increases as the acidity of the solution decreases, and therefore, the ozonation rate of toluene in the aqueous media is much faster than the rate of reaction in carbon tetrachloride and acetic acid by several order of magnitude. A rate constant of 14 $M^{-1}s^{-1}$ for ozonation of toluene in water at 20°C was reported in the literature (29). This value agrees well with the rate constants determined in the present work. A comparison of the kinetic data also suggests that toluene is more reactive with ozone in the aqueous phase than in the vapor phase.

OZONATION OF NAPHTHALENE

It has been suggested in the literature (14,34,35) that two moles of ozone are required to react with one mole of naphthalene to form a diozonide. Bailey (4,5) confirmed the attack of the ozones on 1,2- and 3,4- bonds of naphthalene (the bonds with the lowest bond-localization energy) from a product analysis of ozonolysis of naphthalene in methanol. Since the

intermediate steps for electrophilic addition occur very rapidly, it is likely that the overall reaction is controlled by the initial attack of the ozone molecules. Therefore, the overall reaction can be considered second order with first order each in ozone and naphthalene concentrations. Analyses of the absorbance data obtained in the present work (33) tend to support the second order kinetics for the reaction between ozone and naphthalene in the aqueous phase.

Since the initial concentrations of naphthalene and ozone were in the same order of magnitudes, equations (16) and (20) were applied to correlate the kinetic data using the stoichiometric ratio of 2. Average second order rate constants were summarized in Table 4. Standard deviations range from 10 to 27% in these correlations. It should be noted that the stoichiometric ratio of 3 also was suggested by some earlier investigators (34,35). Calculated results (33) indicate that the differences in the rate constants are insignificant for the stoichiometric ratios of 2 and 3.

The experimental results revealed that the acidity of a solution was an important factor affecting the reaction rate. The reaction in the neutral solutions was faster than that in the acidic solutions as can be seen from Table 4. Temperature is another factor influencing the ozonation rate. For example, the rate constant increases from 848 to 9845 1/M-s or about 10 times for a temperature increase of 10^{o} from 25 to 35°C in the acidic solutions with the pH value of 3.

TABLE 4. AVERAGE RATE CONSTANTS FOR THE NAPHTHALENE-OZONE REACTION

pH value	TEMP, °C	RATE CONSTANT, 1/M-s
3	25	848
3	35	9845
5.6	25	3202
7	25	3749

The simplest molecules of polycyclic aromatic hydrocarbons, naphthalene appears to be more reactive than simple aromatic hydrocarbons such as benzene and toluene with ozone in the aqueous phase. For the ozonation of toluene in the neutral solutions at 25°C, for example, the average second order rate constant can be calculated to be about 173 1/M-s. This value is much lower than the rate constant of 3749 1/M-s obtained for the ozonation of naphthalene at the same condition. In the acidic solutions with a pH value of 3, the rate constants for the ozonation of toluene and naphthalene are 27 and 848 1/M-s, respectively, at 25°C. Again, this shows that the rate of ozonation of naphthalene was much faster than that of toluene. This conclusion is in agreement with the literature report that polycyclic aromatic compounds are, in general, more reactive than simple aromatic hydrocarbons.

OZONATION OF PHENANTHRENE

Since the solubility of phenanthrene in aqueous media is very low at room temperature (7×10^{-6} gmole/l or less), the experiments were conducted with dissolved ozone in large excess in the solutions. Absorbance behaviors during the reaction and various methods for analysis of the absorbance data were discussed in a recent publication (10). The correlations indicated that the

reaction was first order with respect to concentrations of both phenanthrene and ozone. As listed in Table 5, the average rate constants range between 14,600 and 101,300 1/M-s indicating that the phenanthrene was reactive with ozone in aqueous media. The half life of reaction varied from about 0.1 to 1 seconds in the experiments. At 25°C with an initial ozone concentration of $1x10^{-4}$M, for example, the half reaction life decreased from 0.36 to 0.15 seconds as the pH value increased from 2.2 to 7.0.

The effect of acidity on the reaction rate constant is indicated in Figure 14. The rate constant increases with the pH value but the rate of increase is much more pronounced at 35°C than at 15°C. At 35°C, the rate constant varies from about 20,000 to 101,300 1/M-s in the pH range of 2 to 7. On the other hand, the rate constant increases from about 10,000 to 26,000 1/M-s at 15°C in the same pH range. It should be noted that rate constants reported in a recent paper (9) for two pH values at 25°C agree fairly well with our results. The observation in the publication regarding insignificant influence of acidity on the reaction rate, however, is not supportable from the findings of the present work.

The Arrhenius equation can be applied to correlate the dependence of the rate constant on temperature as shown in Figure 15. Activation energies of the reaction are estimated to be about 7 kcal/mole at the pH value of 3, and 12 kcal/mole at pH values of 5.8 and 7. The calculated activation energies and rate constants suggest that phenanthrene was more reactive than some simple aromatic compounds with ozone in aqueous media. The slight change in the activation energy with the acidity might be indicative of some differences in the reaction mechanisms between the phenanthrene and ozone at various acidities. The differences in absorbance behavior in acidic and neutral solutions also were noted earlier. However, judging from the fact that the

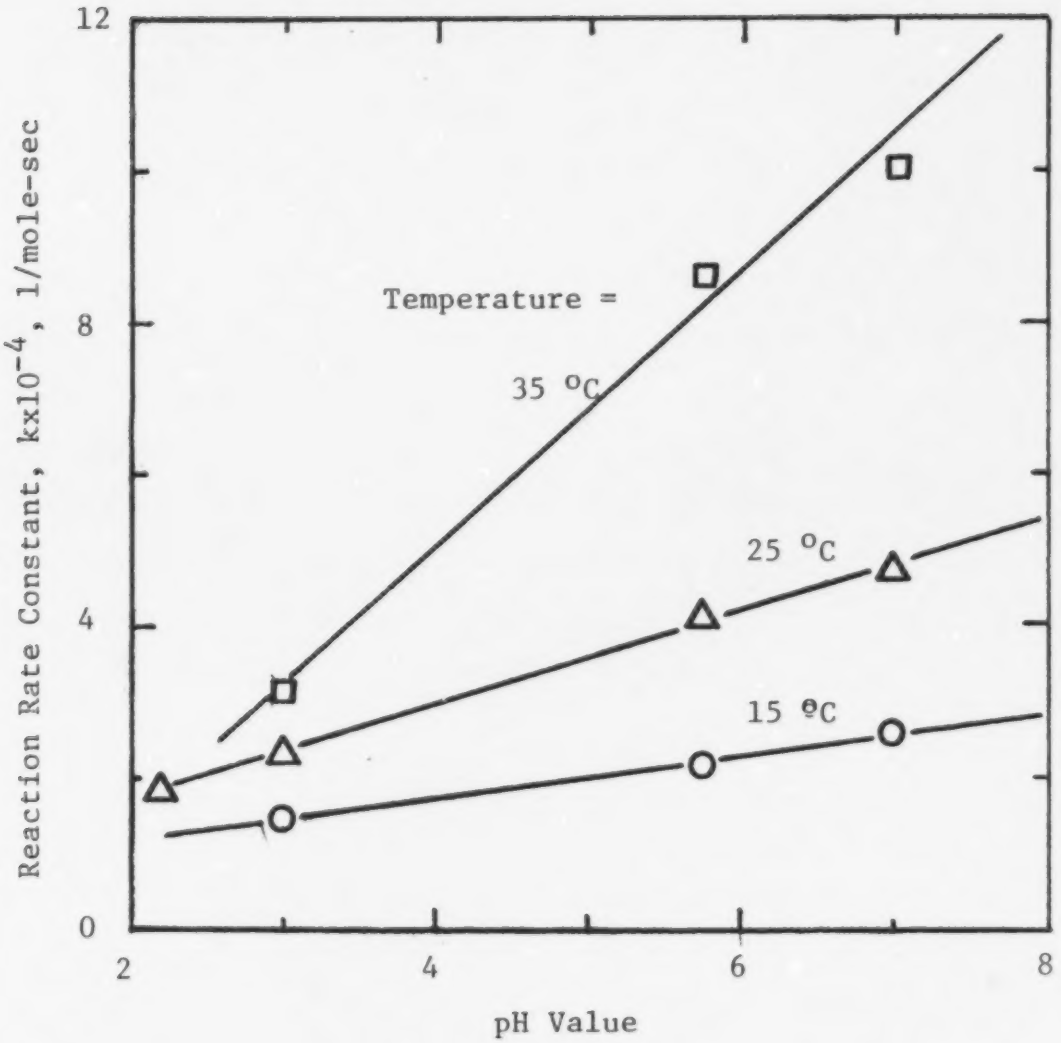


Figure 14. Effect Of Acidity On The Phenanthrene - Ozone Reaction

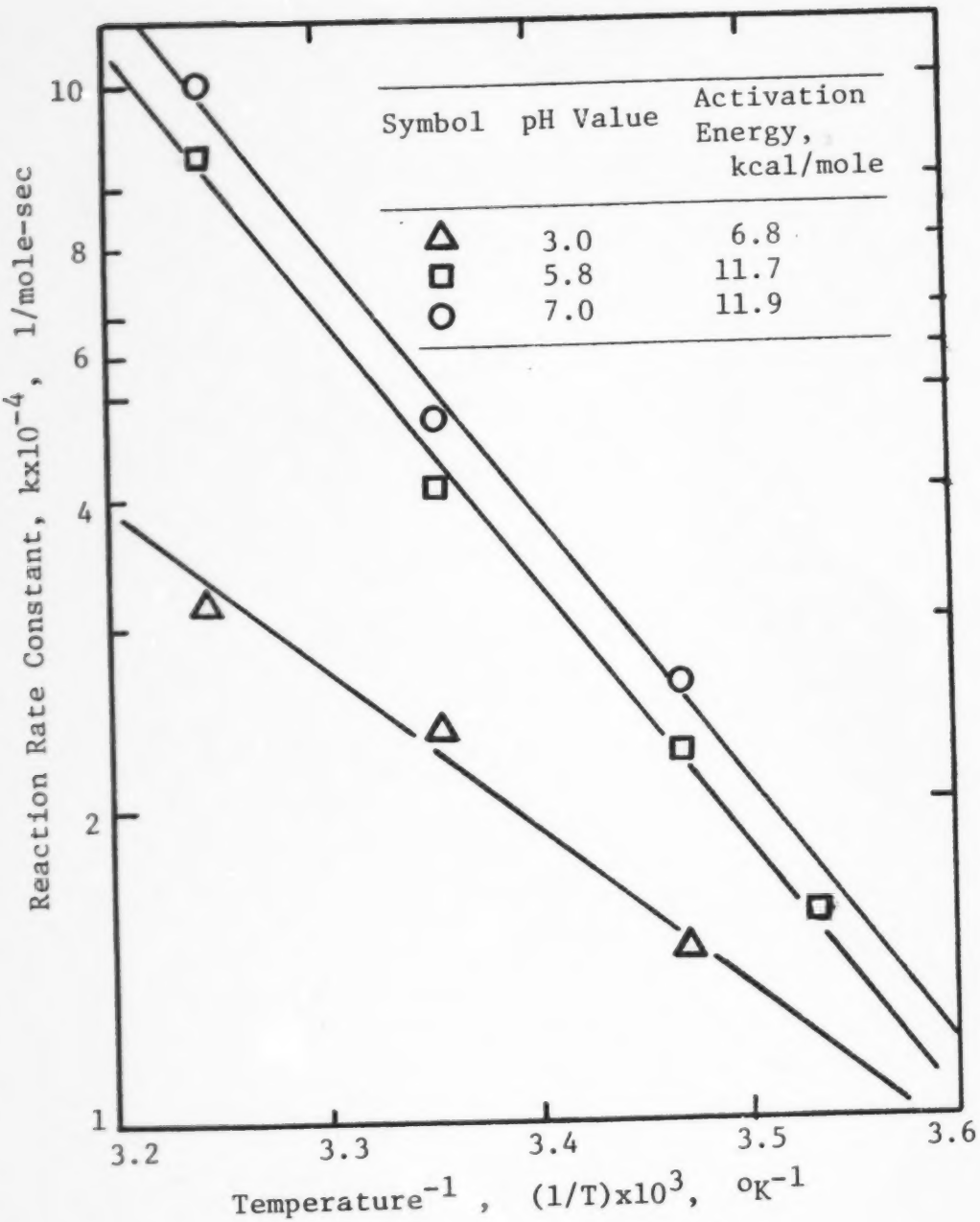


Figure 15. Effect Of Temperature On The Phenanthrene - Ozone Reaction

overall kinetics of the reaction can be treated as second order in all aqueous solutions, the differences in the reaction mechanisms at various acidities might be of a minor nature. Therefore, the conclusion regarding the major reactions of phenanthrene by ozonolysis at the 9,10-bond by the previous investigations (8,27,32) appears reasonable. The results of the above investigation were discussed in details in the recent publication(10).

Table 5. Average Rate Constants for the Phenanthrene-Ozone Reaction

pH value	Temperature, ^{o}C	Rate Constant, 1/M-s
2.21	25	19,371
3.00	15	14,578
3.00	25	23,672
3.00	35	31,515
5.75	10	15,676
5.75	15	22,312
5.75	25	40,820
5.75	35	86,232
7.0	15	26,157
7.0	25	47,468
7.0	35	101,332

OZONATION OF ANTHRACENE

Similar to phenanthrene, the solubility of anthracene in water is very low (22,31), and the kinetic experiments were carried out in aqueous solutions

with ozone in large excess. Regression analysis confirmed that the overall reaction was second order with first order each in ozone and anthracene concentrations (23). Average rate constants for the reaction are listed in Table 6.

In the aqueous solution with the average pH value of 2.2, the second order rate constants increase slightly from 1.87×10^7 to 2.68×10^7 1/M-s as the temperature increases from 6 to 35°C. The Arrhenius equation can be employed to correlate the dependence of the rate constant on the temperature as demonstrated in Figure 16. The activation energy can be calculated from the slope of the straight line in the figure to be 2.5 Kcal/gmole and the frequency factor is estimated to be 1.72×10^9 1/M-s. The influence of temperature on the rate of the ozonation of anthracene seems to be unimportant in comparing with the ozonation rate of many other aromatic hydrocarbons. The rate constants for the experiments conducted in both the buffer solutions and distilled water of different pH values at the same temperature of 25°C are nearly identical. The deviation among the average rate constants is less than 10%. These results tend to indicate that the acidity of the aqueous media is not a significant factor in controlling the ozonation rate because of the highly reactive nature of anthracene by ozone attack. This same phenomenon was observed in studying the very fast reaction of cyclohexene with ozone in aqueous solutions as discussed in a previous work (15,16). Although the molecular weight of anthracene is identical to that of phenanthrene, their rates of ozonation were quite different.

The half reaction life of anthracene varied from 0.13 to 1.1 milli-seconds in the experiments. On the other hand, the half life of phenanthrene was about 0.1 to 1.0 seconds as reported earlier. The reaction of anthracene with ozone was much faster than the phenanthrene-ozone reaction in the aqueous

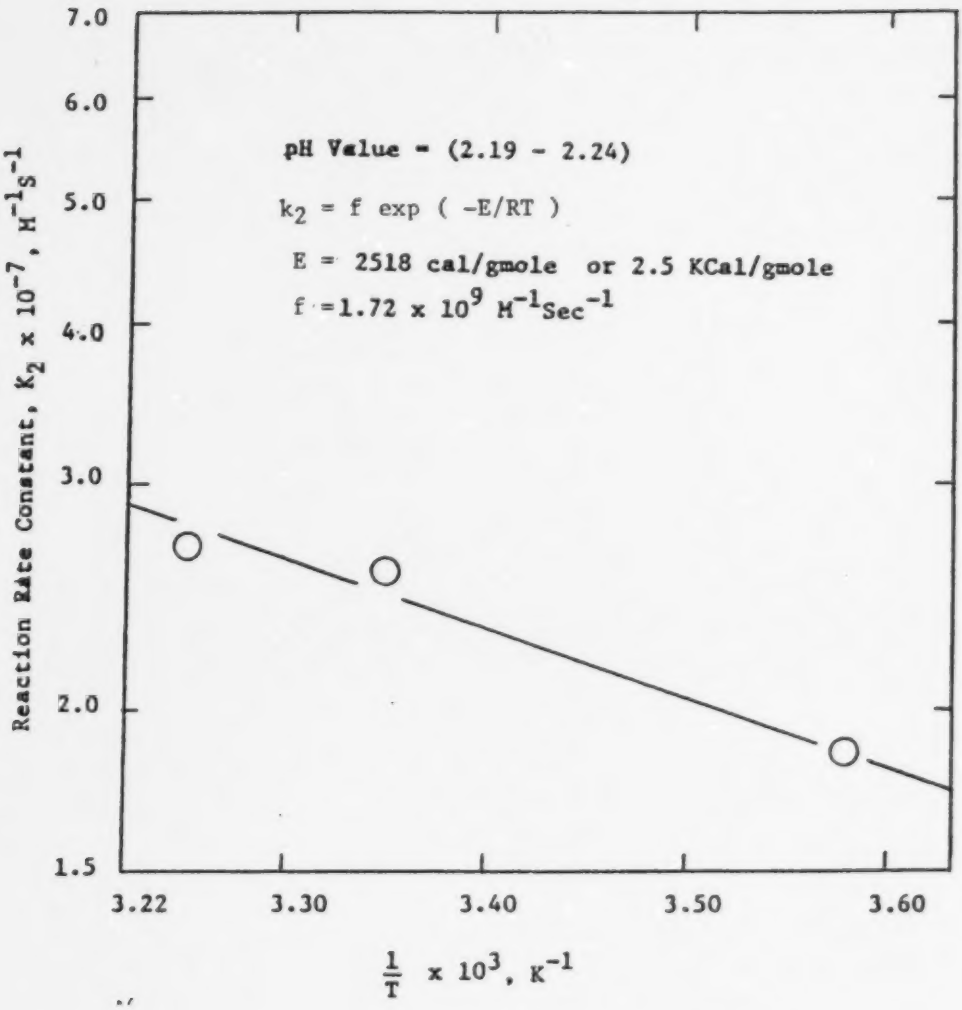


Figure 16. Effect Of Temperature On The Anthracene - Ozone Reaction

media. This might be attributable to the difference in molecular structures of the two compounds though the major attack of ozone seemed to occur at 9, 10 carbon positions of both phenanthrene and anthracene. An electrophilic reagent, ozone attacks carbon atoms 9 and 10 of anthracene which are the positions not only of lowest atom-localization energy, but also of lowest para-localization energy. Three moles of ozone were consumed per mole of anthracene to yield anthraquinone (6,7,11,27). In the case of phenanthrene, the ozone attack resulted in the cleavage of phenanthrene - like double bonds at 9,10-positions. This was a bond of lowest bond - localization energy. This resulted in the formation of diacids, and only one mole of ozone was required for each mole of phenanthrene(8,27).

The 1,2-bond of anthracene represents the bond of lowest bond - localization energy. Instead of this bond, the major ozone attack occurred at the 9,10-atom positions. As indicated by the results of experiments conducted in organic solvents (6,7), the attack at the position of lowest atom-localization and para-localization energy was much more efficient than the attack at the position of lowest bond-localization energy. The experimental evidences from this work suggested that the rate of ozonation of anthracene was much faster than the rate of ozonation of phenanthrene. For example, the rate constant of 2.78×10^7 1/M-s for the anthracene-ozone reaction in distilled water at 25°C is about 700 times larger than the rate constant of 4.1×10^4 1/M-s for the phenanthrene-ozone reaction at the similar condition. Even though both anthracene and phenanthrene have very low solubilities in water, their absorbance behaviors followed different trends. For the ozonation reaction of anthracene, the absorbance of a mixed solution increased rapidly in the initial period then declined very slowly during the remaining life of the reaction. However, in the case of phenanthrene-ozone

reaction, the absorbance declined sharply in the early period with reaction time and approached an asymptotic value as discussed earlier.

The second order rate constants for the reactions of pyrene, phenanthrene and benzo (a) pyrene with ozone in water at 25°C are about 4.0×10^4, 1.5×10^4 and 0.6×10^4 1/M-s, respectively, over the pH range of 1 to 7 (9). The reaction rate constants for ozonation of benzene, toluene, naphthalene, phenanthrene and anthracene in the aqueous media have been obtained in this and previous studies. Among the above organic compounds, anthracene was found to be the most reactive with ozone in the aqueous phase. The reactivity trend for the aromatic hydrocarbons investigated in this and previous projects can be summarized in the following manner:

Anthracene > Phenanthrene > Naphthalene > Toluene > Benzene

TABLE 6. Average of Rate Constants for the Anthracene-Ozone Reaction

pH Value	Temp, C	Rate Constant, 1/M-s
2.19-2.24	6.0	1.87
	25	2.57
5.10	25	2.78
distilled water	35	2.68

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